

MEMORANDUMENVIRONMENTAL
PROTECTION AGENCY

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1080152 - R8 SDMS

TO: Dave Smith
FROM: Chris Cosentini *CC*
DATE: February 3, 2006

CLIENT: Dave Smith, BNSF
TASK: Somers, MT - TI
RE: Evaluation of Natural Attenuation
Rate

Overview

Recent evaluation of groundwater data from the current treatment system at the site indicates that full aquifer restoration as defined in the ROD cannot be achieved in a reasonable timeframe. After six years of operation, the groundwater treatment system has removed only 2% of the estimated DNAPL contamination in the site aquifer. Modeling results estimate that it will take at least 1,700 years of operation to restore the aquifer to drinking water quality. These findings and recommendations for the technical impracticability for groundwater restoration were presented to EPA in April 2003 in the document, *Technical Impracticability Evaluation for Groundwater Restoration, Former Somers Tie Treating Plant, Somers, Montana* (RETEC, 2003). This memo presents an approach to evaluate the assimilative capacity of the aquifer to naturally degrade dissolved phase constituents in groundwater. This capacity can then be compared with removal estimates from the groundwater treatment system.

Evaluation Approach

In order to evaluate the natural biodegradation of the dissolved hydrocarbon plume at the site, calculations will be performed to estimate the rate of naphthalene biodegradation occurring under ambient conditions. This evaluation will be undertaken using the screening methodology described in EPA's document, *BIOSCREEN Natural Attenuation Decision Support System, User's Manual Version 1.3* (Newell, C.J. et al, 1996). For this evaluation, both aerobic and anaerobic biodegradation processes will be simulated as "instantaneous" reactions that are limited by the availability of electron acceptors. This assumption is usually valid in groundwater systems since the microbial reactions occur at much faster rates than the time required for the aquifer to replenish the electron acceptors. This assumption is considered valid for the Somers site since the average linear velocity of groundwater is only approximately 0.007 feet per day (assuming an average hydraulic conductivity of 0.35 ft/day, and a maximum hydraulic gradient of 0.005 ft/ft, and a porosity of 0.25). Another simplification of this method is that it lumps all biodegradation reactions together; that is, it assumes that all of the various aerobic and anaerobic reactions occur over the entire plume. This assumption is also valid at most sites due to hydrogeologic heterogeneity and the existence of biogeochemical "microenvironments" within dissolved contaminant plumes. The effects of this simplification are discussed in Newell et al (1996).



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The electron acceptor limited instantaneous model is applied by calculating the amount of biodegradation able to be supported by the flow of groundwater and flux of electron acceptors through the source zone. The approach to this calculation includes:

- Estimating the total amount of available electron acceptors by calculating the difference between upgradient and source-zone concentrations of oxygen, nitrate, and sulfate and measuring the production of the metabolic by-products ferrous iron and methane in the source zone
- Developing a contaminant utilization factor based on the stoichiometric ratio for the reaction of electron acceptors (oxygen, nitrate, and sulfate) with representative dissolved organic constituents
- Developing a contaminant utilization factor based on the stoichiometric ratio for the production of metabolic by-products (ferrous iron and methane) resulting from biodegradation reactions

Input Data Collection

Concentrations of electron acceptors and metabolic by-products will be taken from existing groundwater monitoring wells. A one time monitoring event is proposed for this initial evaluation. Groundwater samples will be collected using low-flow methodology (SOP 235, attached) from monitoring wells upgradient of the source zone, within the source area and downgradient of the source zone. Low flow sampling will be conducted with a peristaltic pump and field parameters listed on Table 1 will be measured with a flow through cell water quality meter. Groundwater samples will be analyzed for natural attenuation parameters listed on Table 1.

Groundwater monitoring wells were chosen based on the groundwater flow shown in Figure 1. The groundwater elevation data in Figure 1 were collected during a time period when the groundwater treatment system was not operating. Upgradient wells, proposed for monitoring are: S-4, S-85-11, S-85-3, S-87-7, S-85-8a, S-85-8b and S-88-8c. Monitoring wells S-93-5S, S-93-2S, S-93-2D, S-93-3, S-88-1 and S-88-2 are located within the source zone. Monitoring wells S-91-2, S-88-3, S-84-15, S-85-6a and S-85-6b are proposed for sampling to evaluate the influence of natural attenuation on the downgradient edge of the groundwater plume.



Data Evaluation

Utilization of electron acceptors (oxygen, nitrate, and sulfate), or production of metabolic by-products (ferrous iron and methane) will be based on the difference between the upgradient and in-plume concentrations of these parameters. The data will be evaluated to calculate ranges for the measured differences between upgradient and in-plume concentrations of input parameters. A sensitivity analysis will be conducted using the range of concentrations. The sensitivity analysis will be used to evaluate the maximum and minimum aquifer biodegradation capacity as well as evaluate the relative contribution of each parameter to the aquifer biodegradation capacity. Other data required for the calculation include the width of the site, the aquifer thickness, and the average hydraulic conductivity and hydraulic gradient for the site.

Using the parameter concentrations, the site-specific hydrogeologic parameters, and the stoichiometric utilization factors provided in Newell et al. (1996) converted for naphthalene, the data will be input into the attached spreadsheet (Table 2) and the range of total naphthalene assimilative capacity under ambient conditions will be estimated for the site. The range of results can then be compared to the removal estimates from the groundwater treatment system to evaluate the effectiveness of natural biodegradation as a groundwater remedy for the site in the absence of active groundwater extraction and treatment.

TABLE 1**Proposed Biodegradation Capacity Evaluation Parameters and Analytical Methods
Somers, Montana**

Data Requirement	EPA/ASTM Method	Field or Lab	Minimum Sample Size	Number of Containers Per Sample	Container Type/Size	Sample Preservation	Holding Time
Dissolved Oxygen	EPA 360.1	Field	NA	NA	NA	NA	NA
Temperature	NA	Field	NA	NA	NA	NA	NA
Conductivity	NA	Field	NA	NA	NA	NA	NA
pH	EPA 150.1	Field	NA	NA	NA	NA	NA
Oxidation/Reduction Potential	NA	Field	NA	NA	NA	NA	NA
Nitrate	EPA 353.2, EPA 352.1	Pace	100 ml	1	poly/glass	H ₂ SO ₄ to pH<2	28 days
Sulfate	EPA 300.0	Pace	100 ml	1	poly/glass	Cool, 4°C	28 days
Ferrous Iron (unfiltered)	SM3500-FeD#4	Pace	100 ml	1	poly	Cool, 4°C	48 hours
Dissolved Gases (N ₂ , O ₂ , CO, CO ₂ , CH ₄ *)	MS GC-Thermal	Microseeps	40 ml	2	VOA vial	Cool, 4°C	14 days

Notes:

NA - Not applicable

MS - Microseeps analytical method

Field - Field measurement

Pace - Laboratory analysis by Pace Analytical Services, Inc.

Microseeps - Laboratory analysis by Microseeps

poly - Polyethylene sample container

glass - Glass sample container

Table 2
Biodegradation Capacity Evaluation
Somers, Montana

Aquifer Data	Oxygen Flux	Nitrate Flux	Ferrous Iron Flux	Sulfate Flux	Methane Flux
Width of Site (ft)	900 ft				
Aquifer Thickness (ft)	35 ft				
Hydraulic Conductivity (K) (ft/d)	0.35 ft/d				
Gradient (i) (ft/ft)	0.005				
Upgradient Oxygen Conc. (mg/L)	0.5 mg/L	delta NO ₃ 1 mg/L	delta Fe+2 1 mg/L	delta SO ₄ 1 mg/L	delta CH ₄ 1 mg/L
Upgradient Oxygen Conc. (mg/m ³)	500 mg/m ³	1000 mg/m ³	1000 mg/m ³	1000 mg/m ³	1000 mg/m ³
Q=KiA (ft ³ /d)	55.125 ft ³ /d				
Q=KiA (m ³ /d)	1.56 m ³ /d				
Flux of Oxygen [upgradient or delta * Q (in m ³ /d)]	780 mg/d	NO ₃ Flux 1561 mg/d	Fe+2 Flux 1561 mg/d	SO ₄ Flux 1561 mg/d	CH ₄ Flux 1560.97 mg/d
Biodegradation Assimilative Capacity [Flux/utilization factor]	260 mg/d	334 mg/d	75 mg/d	348 mg/d	2109 mg/d
Ambient Naphthalene Biodegradation Capacity (mg/d)	260 mg/d	334 mg/d	75 mg/d	348 mg/d	2,109 mg/d
					Total Assimilative Capacity 3,126 mg/d

Notes:

Naphthalene Utilization Factors*

	mg/L	mg/m ³
Oxygen	3.00	3,000
Nitrate	4.68	4,680
Ferrous Iron	20.8	20,820
Sulfate	4.49	4,490
Methane	0.74	740

	Kg/yr	lb/yr
O ₂	0.09496	0.209349149
Total	1.1409	2.51525607

* = Based on BTEX utilization factor (from BIOSCREEN) corrected for naphthalene by multiplying by 0.955 (or 95.5% of the BTEX utilization factor)

RETEC Standard Operating Procedure (SOP) 235

Low Flow Groundwater Sampling

1.0 Purpose and Applicability

The RETEC Group, Inc. (RETEC) SOP 235 describes methods used to obtain the collection of valid and representative groundwater samples from monitoring wells utilizing a low flow sampling technique. This technique is designed to reduce the influx of particulate matter into the well and groundwater sample to ensure a more representative analysis of groundwater quality, and to reduce aeration that can affect geochemical parameters.

Specific project requirements as described in an approved Work Plan, Sampling Plan, Quality Assurance Project Plan, Job Hazard Analysis (JHA), Safety Task Analysis Review (STAR), or Site-Specific Health & Safety Plan (HASP) will take precedence over the procedures described in this document.

2.0 Responsibilities

The field sampling coordinator will have responsibility to oversee and ensure that all groundwater sampling is performed in accordance with the project specific sampling program and this SOP. It shall be the responsibility of the field sampling coordinator to observe all activities pertaining to sampling to ensure that all the standard procedures are followed properly, and to record all pertinent data on a field log or field book. The collection, handling, and storage of all samples will be the responsibility of the field sampling coordinator. In addition, the field sampling coordinator must ensure that all field workers are fully apprised of this SOP.

3.0 Health and Safety

This section presents the generic hazards associated with low flow groundwater sampling and is intended to provide general guidance in preparing site-specific health and safety documents. The site-specific HASP, JHA, and STAR will address additional requirements and will take precedence over this document. Note that low flow groundwater sampling usually requires Level D personal protection unless there is a potential for exposure to airborne site contaminants.

Health and safety hazards include but are not limited to the following:

- Slip, trips, and falls in tall grasses over obstacles and berms near well locations. Review terrain hazards prior to conducting these operations. Ensure there is a safe means of access/egress to the wellhead.

- Dermal exposure to potentially contaminated groundwater. Ensure that proper personal protective equipment (PPE) is used to mitigate the impact of splashes of groundwater to skin and/or eyes.
- Exposure to site contaminants. If there is product in the well (especially gasoline) take all precautions necessary to prevent fire/explosion and/or exposure to airborne vapors.
- Ergonomics. Use appropriate ergonomic techniques when inserting or retrieving equipment for the wells to preclude injury to the arms, shoulders or back.

4.0 Supporting Materials

The following list of equipment will be used to determine the depth to water, purged volume, and analytical parameters.

Sampling/Purging Equipment

- Low flow submersible bladder pump or peristaltic sampling pump
- Teflon and polyethylene tubing
- Water level measurement equipment

Field Analytical Parameter Measurement

- In-line water quality meter (e.g., flow-through cell)
- Water quality meter with individual temperature, pH, specific conductance, dissolved oxygen (DO), turbidity, salinity, and oxidation reduction potential (ORP) probes
- Turbidity meter

Supporting Documents

- Project specific Work Plan
- Material Safety Data Sheets (MSDSs) for any chemicals or site-specific contaminants
- A copy of the Site-Specific HASP
- Field data sheets and log book

Decontamination Equipment

- Distilled water
- Isopropanol (laboratory grade)
- Spray bottles for decontamination solutions
- Chemical free paper towels

Sample Collection

- Preservation solutions (if necessary)
- Sample containers
- Coolers

Peristaltic Pump Sample Collection

- Generator and extension cord
- Battery packs

Bladder Pump Sample Collection

- Dedicated bladders
- Pump controller box
- Nitrogen (air supply)
- Detergent/Alconox
- Nitric or hydrochloric acid (laboratory grade)
- Cleaning brushes

Miscellaneous

- Disposable gloves
- Tubing cutters
- Plastic sheeting
- PPE
- Buckets and intermediate containers

5.0 Methods and Procedures

The following sections describe the methods and procedures required to collect representative groundwater samples.

5.1 Water Level Measurement

After unlocking and/or opening a monitoring well, the first task will be to obtain a water-level measurement. A static-water level will be measured in the well prior to the purging and collection of any samples. The water level is needed for estimating the purge volume

and may also be used for mapping the potentiometric surface of the groundwater. Water-level measurements will be made using an electronic or mechanical device following the methods described in SOP 231.

Measurement of point location for the well should be clearly marked on the outermost casing or identified in previous sample collection records. This point is usually established on the well casing itself, but may be marked on the protective steel casing in some cases. In either case, it is important that the marked point coincide with the same point of measurement used by the surveyor. If not marked from previous investigations, the water level measuring point should be marked on the north side of the well casing and noted in the groundwater sampling form (Figure 1). Whatever measuring point is used, the location should be described on the groundwater sampling form.

To obtain a water level measurement lower a decontaminated mechanical or an electronic sounding unit into the monitoring well until the audible sound of the unit is detected or indicates water contact. At this time the precise measurement should be determined by repeatedly raising and lowering the tape or cable to converge on the exact measurement. The water-level measurement should be entered on the groundwater sampling form. The water-level measurement device shall be decontaminated immediately after use following the procedures outlined in RETEC SOP 120 (Decontamination).

5.2 Purging and Sample Collection

5.2.1 Pumping

Purging must be performed for all groundwater monitoring wells prior to sample collection. The volume of water present in each well must be computed using two measurable lengths, length of water the water column and monitoring well inside diameter. A low flow, electric driven pump (e.g., bladder pump or peristaltic pump) will be used to purge and sample well water.

The inlet of the bladder pump or peristaltic pump tubing will be lowered into the well slowly and carefully to a depth corresponding with the approximate midpoint of the screened interval of the aquifer, or 1-2 feet below the water level in the well, whichever is greater. A depth-to-water measurement device will be lowered into the well to monitor drawdown. The pump will be turned on at a flow rate of about 0.1 liters per minute (L/min). The flow rate will be adjusted up or down to maximize flow, yet ensure minimum drawdown. In no instance should a drawdown of more than 0.5 foot be allowed. The water level in the well should be carefully monitored to ensure that draw down does not increase during purging.

If the well being sampled is newly installed and developed or has been redeveloped, sampling can be initiated as soon as the groundwater has re-equilibrated, is free of visible sediment, and the water quality parameters have stabilized. Since site conditions vary, even between wells, a general rule-of-thumb is to wait 24-hours after development to sample a new monitoring well. Wells developed with stressful measures (e.g., backwashing, jetting, compressed air, etc.) may require as long as a 7-day interval before sampling.

5.2.2 Field Parameters

Groundwater will be pumped from the well into a sealed, flow-through chamber containing probes to measure the water temperature, pH, turbidity, conductivity, ORP, and DO using a Water Quality Meter. Field measurements of turbidity will also be obtained using a turbidity meter for comparison purposes. It is essential to properly calibrate the Water Quality Meter for the specific parameters being monitored, according to the procedures identified in the instrument manual. Calibration procedures and results must be documented in the site field notebook.

Field parameters values will be recorded on the Groundwater Sample Collection Record (Figure 1) or in the site field notebook along with the corresponding purge volume. After passing through the flow-through chamber, the water will be discharged into a container of known volume where the pumping rate will be measured with a watch. When the container is full, the water will be properly disposed following Site protocols.

Groundwater samples will be collected for laboratory analysis when the groundwater has stabilized; the change between successive readings of temperature, pH and conductivity are less than 10%, and turbidity is reduced to 10 NTUs or less. This may occur prior to removal of three well volumes. Stabilization of groundwater measurements are considered indicative of sampling fresh formation water and is a more reliable indicator of purging than removal of a standard volume of water.

5.2.3 Decontamination

Decontamination of non-dedicated equipment will follow the procedures outlined in RETEC SOP 120 (Decontamination), or following the procedures listed below for full field decontamination, conducted in the order presented:

- Remove gross contamination from the equipment by brushing or steam cleaning
- Wash with non-phosphate soap/detergent solution
- Rinse with laboratory-grade nitric acid (for potential inorganic contamination)
- Rinse with tap water
- Rinse with laboratory grade isopropanol
- Rinse with tap water
- Rinse with distilled water
- Allow to air dry
- Repeat as necessary

Teflon tubing will be dedicated to each well and will, therefore, not require decontamination.

5.3 Sample Preparation

Proper packaging and shipment of samples will minimize the potential for sample breakage, leakage, or cross contamination and will provide a clear record of sample custody from collection to analysis. Information on sample custody and shipping is also

detailed in RETEC SOP 110 (Packaging and Shipment of Samples). Samples will be packaged on ice and shipped in a container able to maintain a temperature at or below 4°C.

6.0 Quality Assurance/Quality Control

Quality Assurance/Quality Control (QA/QC) requirements include, but are not limited to, blind field duplicates, blind rinsate blanks, and blind field blanks. These samples will be collected on a frequency of one QA/QC sample per 20 field samples or a minimum of one QA/QC sample per day unless otherwise specified in the project specific sampling plan.

7.0 Documentation

The groundwater sampling program will be documented to provide a summary of the sample collection procedures and conditions, shipment method, the analyses requested and the custody history. Such documentation shall include:

- Field notebook
- Groundwater sample collection record
- Sample labels
- Chain-of-custody forms
- Shipping receipts
- Health & Safety forms (JHA, STAR, and/or Site-Specific HASP amendments)

All documentation shall be placed in the project files and retained following completion of the project.

The RETEC Group, Inc.
Groundwater Sampling Form

PROJECT _____ WELL NO. _____
PROJECT NO. _____ SAMPLERS _____

1. WELL CONDITION CHECKLIST:

- a. Bump posts _____ Prot. casing/lock _____ Surface pad _____
b. Well visibility (paint) _____
c. Well label _____

2. WATER LEVEL MEASUREMENT:

DATE _____ TIME _____

WEATHER CONDITIONS _____

- a. Location of measuring point _____
b. Depth of water table from measuring point _____
c. Height of measuring point above ground surface _____
d. Total depth of well below measuring point _____
e. Length of water column (line 2d-2b) _____

3. WELL PURGING:

DATE _____ TIME _____

WEATHER CONDITIONS _____

- a. Purge method _____
b. Required purge volume at 3 well volumes _____

Pumping Duration	Volume Rmvd.	pH	Redox	Cond.	T(C)	Color	Turbidity
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4. SAMPLE COLLECTION:

DATE _____ TIME _____

WEATHER CONDITIONS _____

- a. Collection method _____
b. Meter calibration _____ Date _____ Model _____
 pH meter _____
 D.O. meter _____

c. Sample information pH _____ Cond. _____ T(C) _____ Turbidity _____

Analysis	Containers	Sample Prep./Preservation
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d. Chain of custody form _____ COC tape _____

e. Shipping container _____

5. COMMENTS:

File: J:\1860\240\NAM_FIG1.dwg Layout: Layout1 User: mwilliamson Plotted: Feb 02, 2006 - 3:17pm Xref's:

